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(54) PRODUCTION OF CARBONACEOUS FIBER

(57)Abstract:
PROBLEM TO BE SOLVED: To deposit fibrous carbon at a selectively necessary spot on a substrate.
SOLUTION: In making graphite fiber by chemical vapor growth process using, as raw material 1, an organometallic compound containing metallic atom serving as catalyst as a constituent, a material poor in reactivity is used as a substrate, and carbon or metal is made to adhere, in advance, to a specific spot on the surface of the substrate.

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CLAIMS

[Claim(s)]

[Claim 1] The creation approach of the carbonaceous fiber characterized by in creating a graphite fiber by the chemical-vapor-deposition method by using as a raw material the organic metal compound which contains the metal used as a catalyst as a component using the scarce matter for reactivity as a substrate, and making carbon or a metal adhere to the specific location on the front face of a substrate beforehand.

[Claim 2] The carbon or the metal made to adhere to a substrate front face beforehand is the creation approach of the carbonaceous fiber according to claim 1 which has the shape of the shape of a thin film, and a particle.

[Claim 3] The metal made to adhere to a substrate front face beforehand is the creation approach of a carbonaceous fiber of having described it having been the metal of the another kind which does not make stoichiometric metallic carbide the same as that of the metal atom contained as a component of the organic metal compound which is a raw material, or stable in claim 1 by which it is characterized.

[Claim 4] The creation approach of a carbonaceous fiber according to claim 1 of being the layered product of the layer of the carbon with which a substrate adheres on a substrate beforehand thru/or a metal, and

the layer of the matter lacking in the reactivity which constitutes a substrate, removing a part of layer of the scarce matter to the reactivity of the outermost superficial layer of this layered product, and exposing the layer of carbon thru/or a metal to it.
[Claim 5] The creation approach of a carbonaceous fiber according to claim 4 of having removed a part of layer of the 2nd carbon thru/or a metal with a part of layer of the scarce matter to the reactivity of the maximum upper layer.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the approach of depositing fiber-like carbon in a location required for especially a selection target, about creation of the carbon material of the shape of a thin fiber.
[0002]
[Description of the Prior Art] There are an approach of carrying out spinning of the organic substance first, making it the shape of a fiber as an approach of creating the fiber of a carbon material, and heat-treating this at an elevated temperature and a method of using iron for a catalyst and growing up a fiber with vapor growth, and the method of growing up a fiber by arc discharge by using carbon as an electrode is reported recently. In these approaches, by the approach of carrying out spinning of the organic substance and carrying out high temperature processing of this, the approach of creating the fiber of carbonaceous is difficult to control the structure of a carbonaceous ingredient, and the good object made from a crystal is not obtained. By the approach of creating a fiber by vapor growth by making iron into a catalyst, it is reported that the fiber in which a graphite side has the structure rolled in the shape of a concentric circle column is obtained. Recently, this invention person etc. invented the technique of making only the part of the pattern of the nickel formed on the quartz substrate by the gaseous-phase depositing method using a certain kind of raw material generating a carbonaceous fiber (Japanese Patent Application No. No. 210161 [seven to]). This carbonaceous fiber is matter with which it is expected by the slight difference in structure that the broad property

from metallic conductivity to the conductivity like a semi-conductor is shown, and new application is expected.

[0003] However, that the so-called graphite nanotube which the mesh plane of graphite rolled concentrically among the methods of creating the above-mentioned conventional graphite fiber can be made has an approach using iron, and an approach using arc discharge in a catalyst. The approach using iron is an approach of generating an iron particle by gaseous phase reaction, using it as a catalyst in a reaction container as it is, and making a graphite fiber generate using the raw material gas which contained iron as a component, for example, a ferrocene. In order to generate a fiber, the high temperature of 1000 degrees C or more is required of this approach. Moreover, generation of a fiber cannot take place in the space in a coil, and all the parts of a wall surface, cannot be limited to the field to need, and cannot create a fiber.

[0004] Moreover, by the approach by arc discharge, among discharge electrodes, a graphite fiber serves as a lump and it generates only to a cathode side. Therefore, a location required also in this case cannot be made the special equipment for arc discharge to be not only needed, but to generate a fiber. In the approach which this invention person etc. developed, although the fiber could be created locally, there was constraint of that the thickness of that a catalyst ingredient is restricted to nickel or its nickel is restricted extremely, that a fiber generation raw material is restricted to the specific matter, fiber generation temperature being restricted.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention aims at offering the approach formed in the alternative location on a base in the precision below submicron one in a graphite fiber except for the above-mentioned constraint.

[0006]

[Means for Solving the Problem] In creating a graphite fiber by the chemical-vapor-deposition method by using as a raw material the organic metal compound which contains the metal used as a catalyst as a component, the summary of this invention is the creation approach of the carbonaceous fiber characterized by using the scarce matter for reactivity as a substrate, and making carbon or a metal adhere to the specific location on the front face of a substrate beforehand.

[0007]

[Function] In the field which deposited carbon thru/or a metal beforehand on the reactant scarce substrate to depositing nothing on the

exposed substrate front face if carbon thru/or a metal are made to deposit locally and a chemical-vapor-deposition method is applied like the above-mentioned means, the fiber of carbonaceous generates this invention. Thus, according to this invention, the field which needs a substrate can be made to generate a carbonaceous fiber simply. Furthermore, according to this approach, only that part can be made to generate a carbonaceous fiber by covering the front face of carbon thru/or a metal with the thin film of the reactant scarce matter, for example, removing that thin film locally, and exposing a lower layer. For example, when the lower layer was a conductive thing, each carbonaceous fiber should be connected electrically.

[0008] Hereafter, this invention is stated to a detail. The approaches of creating a graphite fiber by the chemical-vapor-deposition method in this invention are cobalt, nickel, iron, or these alloys as a metal which says the pyrolysis and polymerization reaction of a gas-like raw material, and acts on this reaction as a catalyst. In the invention in this application, a source material is an organic metal compound containing the metal used as such a catalyst, and is an organic metal compound which has the vapor pressure suitable for performing CVD. Although a phthalocyanine system compound, a metallocene system compound, etc. containing the metal which specifically serves as a catalyst are mentioned, it is not limited to these. For example, as a source material which contained cobalt as a metal which acts as a catalyst, phthalocyanine cobalt is suitable. This invention creates a carbonaceous fiber by the gaseous-phase depositing method on a substrate using such an organic metal compound. Although the temperature which heats a source material changes with raw materials in that case, usually it is about 300 degrees C - about 1000 degrees C, and it is desirable to heat a substrate, and 750 degrees C or more are desirable 700 degrees C or more especially as the temperature. As an ambient atmosphere of a reaction chamber, the inert atmosphere thru/or vacuum of an argon, nitrogen, etc. is desirable under one atmospheric pressure or reduced pressure.

[0009] Although any are sufficient as it as long as the matter lacking in the reactivity used as a substrate in this invention is matter to which a metal does not react with reaction temperature while not participating in the chemistry gaseous phase reaction of this invention, it is specifically a quartz, an alumina, a silicon oxide, etc. And carbon or a metal is made to adhere to this substrate front face, and a carbonaceous fiber is grown up from this attachment site. The metals when calling it carbon or a metal are transition metals, and iron-group thru/or a platinum group are desirable, and can mention cobalt, platinum,

etc. although especially the metal contained in the organic metal compound which is a raw material as a component and the metal made to adhere on a substrate may differ even if they are the same and, the case of the same metal is desirable and it is desirable to use the phthalocyanine thru/or the similar organic metal compound which contained cobalt as a raw material especially, to use the substrate which adhered cobalt to the substrate, and to create a carbonaceous fiber on this cobalt. Carbon or a metal is made to adhere to the field which is going to make a substrate front face generate a carbonaceous fiber beforehand. As an approach to which carbon or a metal is made to adhere, after forming the layer of a photoresist on a substrate, it carries out by the approach of carbonizing, or making a metal vapor-deposit on a substrate, forming formation, its afterbaking, and the obtained metal membrane for a pattern by the photograph RIZOGURA fee, and forming the shape of **, the shape of a dot, and the required pattern 1 micrometer or less of width of face with the technique of photolithography. In the case of a metal thin film, although especially the thickness is not restricted, in the case of a carbonaceous thin film, 50nm or less is desirable. Moreover, also in a particle, in the case of carbonaceous, it is desirable that size is 50nm or less.

[0010] Furthermore, beforehand, it adheres by turns, the laminating of the layer of carbon or a metal and the layer of the matter deficient in a reaction can be carried out, and the layered product which removed a part of layer of the scarce matter for the reaction of the outermost superficial layer, and exposed the layer of carbon or a metal to it can be used as a substrate. Since a carbonaceous fiber is generated from the carbon of a lower layer, or a metaled layer by using the substrate of such a layered product, if carbon or a metal is a conductive thing, effectiveness -- the carbonaceous fiber connected electrically is obtained -- can be done so.

[0011]

[Working Example(s) and Comparative Example(s)] Hereafter, this invention is concretely explained with an example. Although an example describes the system which mainly contained cobalt, this invention is not necessarily restricted to this.

One or less example and the 1st example of this invention are explained referring to a drawing. Drawing 1 is the mimetic diagram of the process of the graphite fiber creation in one example of this invention. In drawing 1 , the coil 4 was a thing made from a quartz, and in order for a sludge to prevent adhering and deteriorating in the wall of a reaction by the reaction, it laid the liner tubing 41 in the coil 4. Whenever

this liner tubing 41 reacted, it was exchanged for the pure thing. The raw material 1 of CVD was paid to the suitable container 2, and was installed into liner tubing. Phthalocyanine cobalt was used in this example.

[0012] The temperature of a coil 4 was heated with the electric furnace 6, and controlled the evaporation of a raw material 1 by the electric furnace 6. The temperature of the substrate 3 installed into the same liner tubing 41 was controlled by the electric furnace 5. The substrate 3 used here vapor-deposits nickel in thickness of 5nm on quartz glass, and processes it with the technique of photolithography with a width of face of 1 micrometer or less in the shape of a muscle. Moreover, it enabled it to supply high grade argon gas by the rate controller 7 in a coil 4. An exhauster 9 is connected to the exhaust side of a coil 4 through pulp 8, and it enabled it to control the pressure in a coil 4. The temperature of the part which installed the raw material 1 was set as 380 degrees C. It set to the purpose that this temperature evaporated a raw material 1 in suitable vapor pressure. Moreover, the temperature of the substrate installation section was set as 850 degrees C. High grade Ar gas was made to react with a sink and one atmospheric pressure with a rate of 300 cc/m for 1 hour. When microscope observation of this sample was carried out after reaction termination, the carbonaceous fiber 50 micrometers or more was generating die length along with the stripe of nickel by 1 micrometer or less of sizes. On the other hand, nothing was deposited on the exposed quartz.

[0013] When cobalt, iron, platinum, etc. were tried on the quartz substrate as a metal which creates a pattern beforehand, it turned out that a fiber generates any metal. When this fiber was observed with the transmission electron microscope, it turned out that the layer-like graphite side is winding around the concentric circle cartridge, and the center has structure which connoted the cobalt particle in part by hollow. Especially when were changed and seen from 300 degrees C to 1000 degrees C, the temperature, i.e., the reaction salt, of a place which installs a substrate, and phthalocyanine cobalt was used as a raw material, 700 degrees C or more of temperature which a carbon nanotube generates were understood that 800 degrees C or more are desirable. Moreover, when the pressure of the ambient atmosphere under reaction was made into the reduced pressure conditions instead of one atmospheric pressure, even if it lowered to 0.01 atmospheric pressure, the carbon nanotube generated like the case of one atmospheric pressure.

[0014] Two or less example and the 2nd example of this invention are explained referring to a drawing. Drawing 2 is drawing showing the

reactor of one example of this invention, and the evacuation to the pressure of 10~6 pascals is possible for the quartz coil 24 by the exhaust air system 29 containing a turbo molecular pump. The source material 1 and the substrate 3 are installed into this quartz coil 24. This raw material 1 and substrate 3 used the same object as the time of an example 1. After installing a raw material 1 and a substrate 3, it exhausted within the reaction to 10~5Pa first by the exhaust air system. Then, temperature was raised for the substrate 3 to 850 degrees C, exhausting, and the temperature up of the temperature of the raw material section was carried out to 380 degrees C after an appropriate time. The raw material evaporated, it reacted on the substrate, and the resultant accumulated on the low-temperature section of a coil. The deposited object was presenting blue. Reaction time was carried out in 1 hour. The temperature of an electric furnace was lowered after reaction termination, and as a result of taking out and investigating a substrate, it turned out that the carbonaceous fiber is generating like the case of an example 1. When the temperature of the place in which the substrate 1 is installed, i.e., reaction temperature, was changed and seen from 300 degrees C to 1000 degrees C, the temperature which a carbonaceous fiber generates found out that it was 700 degrees C or more, when phthalocyanine cobalt was used as a raw material. When phthalocyanine nickel was used, the carbonaceous fiber generated above 650 degrees C.

[0015] When the plate of an alumina was used instead of example 3 quartz and the same experiment as an example 2 was conducted, the carbonaceous fiber generated only into the part of a metaled stripe similarly.

In example 4 example 2, the dot-like pattern was formed instead of the stripe-like pattern, and the same experiment as an example 2 was conducted except it. Even the pattern considered to be about 1nm from 2 micrometers was able to be made by adjusting the time amount of etching in the case of photolithography. This may consider a particle. When the substrate with such a pattern was used, two or more carbonaceous fibers generated to the big pattern, but when it became small, it turned out that only one fiber generates. Moreover, this showed that the pattern on a quartz was what gives the cause of fiber generation.

[0016] Using a quartz as example 5 substrate, on it, the coat of the photoresist (AZ-1400) was carried out to the thickness of 0.2 micrometers, and the pattern of 1-micrometer width of face was formed with the technique of photolithography. When the same experiment as an example 2 was conducted using what carried out the heating carbonization of the resist pattern on this quartz in the argon air current at 700 degrees C, the fiber grew up to be only the part of the carbonized

resist. However, when thickness of a resist was thickened, it turned out that generation of a fiber is barred rather. Good fiber generation found that it was desirable that the thickness of a resist is 10 micrometers or less. Nothing was generated in the field which the quartz front face exposed in any case of thickness.

[0017] That from which the configuration of a substrate is different as another example of example 6 this invention is explained. Drawing 3 (a) is the sectional view of the structure of the substrate of this example. The metal cobalt layer 32 with a thickness of 250nm is vapor-deposited on the quartz plate 31, and the quartz layer 33 with a thickness of 80nm is formed with plasma vapor growth on it by a diagram. The technique of photolithography removes the quartz layer 33 locally, and it exposes the cobalt layer 32 under it. Although the carbonaceous fiber generated in the front face of the exposed cobalt when reacted by the same approach as an example 2 using such a substrate, nothing was generated on the surface quartz layer. This situation is typically shown in drawing 3 (b).

[0018] Example 7 drawing 4 shows still more nearly another substrate configuration. On the quartz plate 31, the metal cobalt layer 32 with a thickness of 250nm was vapor-deposited by drawing 4 , and the quartz layer 33 with a thickness of 80nm was formed with plasma vapor growth on it. The technique of photolithography removed locally the quartz layer 33 and the cobalt layer 32, and the bottom quartz tabular plane is exposed. That is, there is that the metal is exposed only in the cross-section part of the layer pinched by the quartz. When reacted by the same approach as an example 2 using such a substrate, the carbonaceous fiber generated only on the exposure front face of the narrow cobalt inserted into the quartz, and nothing was generated in the other quartz layer front face. This situation is typically shown in drawing 4 (b).

[0019]

[Effect of the Invention] As mentioned above, this invention gives the approach of making a carbonaceous fiber generating locally, and according to this approach, it can control by precision below submicron one the location which a fiber generates.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing of the equipment used for the carbonaceous fiber

creation in the 1st example of this invention
[Drawing 2] Drawing of the equipment used for the carbonaceous fiber creation in the 2nd example of this invention
[Drawing 3] (a) the structure of the substrate used in the 6th example of this invention, and (b) -- the mimetic diagram showing the generation situation of the carbonaceous fiber when using this substrate
[Drawing 4] (a) the structure of the substrate used in the 7th example of this invention, and (b) -- the mimetic diagram showing the generation situation of the carbonaceous fiber when using this substrate
[Description of Notations]
1 Source Material 2 Raw Material Container 3 Base 31 Quartz Substrate
32 Metal Cobalt Layer 33 Quartz Layer by Plasma CVD
4 Quartz Coil 41 Quartz Liner Tubing 5 Six Electric Furnace
7 Flow Regulator 8 Needle Valve 9 Exhaust